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ECBC-TR-381

FEASIBILITY OF FORMULATING DECON GREEN WITH AIRCRAFT DEICING FLUID: VX, GD, AND HD REACTIVITY



George W. Wagner

GEO-CENTERS, INC. - GUNPOWDER BRANCH

Lawrence R. Procell

RESEARCH AND TECHNOLOGY DIRECTORATE

Joseph B. Kiple, MAJ
Jeffrey S. Taylor

JOINT SERVICE MATERIEL GROUP



Yu-Chu Yang

US ARMY EUROPEAN RESEARCH OFFICE
LONDON, UK

January 2005

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20050413 036



ABERDEEN PROVING GROUND, MD 21010-5424

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REPORT DOCUMENTATION PAGE

Form Approved
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1. REPORT DATE (DD-MM-YYYY) XX-01-2005		2. REPORT TYPE Final		3. DATES COVERED (From - To) Jan 1999 - Jun 1999	
4. TITLE AND SUBTITLE Feasibility of Formulating DECON GREEN with Aircraft Deicing Fluid: VX, GD, and HD Reactivity				5a. CONTRACT NUMBER DAAM01-98-C-0008	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Wagner, George W. (GEO-CENTERS, Inc.);* Procell, Lawrence R. (ECBC); Kiple, Joseph B., MAJ; Taylor, Jeffrey S. (JSMG); and Yang, Yu-Chu (U.S. Army ERO)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) GEO-CENTERS, Inc., P.O. Box 68, Gunpowder Branch, APG, MD 21010-0068 DIR, ECBC, ATTN: AMSRD-ECB-RT-CA, APG, MD 21010-5424 Joint Service Materiel Group, APG, MD 21010 U.S. Army ERO, USARDSG-UK, PSC 802, Box 15, FPO AE 09499-1500				8. PERFORMING ORGANIZATION REPORT NUMBER ECBC-TR-381	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) DIR, ECBC, ATTN: AMSRD-ECB-RT-CA, APG, MD 21010-5424				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES *Currently employed by the Research and Technology Directorate, U.S. Army Edgewood Chemical Biological Center, APG, MD 21010-5424.					
14. ABSTRACT DECON GREEN is a reactive, universal decontaminant for VX, HD, and G agents composed of bicarbonate (baking soda), hydrogen peroxide, and alcohol. The use of two currently fielded aircraft deicing fluids, containing ethylene glycol and/or propylene glycol and water, as substitutes for the alcohol constituent was assessed by examining the VX, GD, and HD reactivity in formulations using these materials.					
15. SUBJECT TERMS					
Decontamination		Aircraft deicing fluid		Perhydrolysis	
DECON GREEN		Oxidation		Peroxide	
				VX	
				GD	
				HD	
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Sandra J. Johnson
U	U	U	UL	11	19b. TELEPHONE NUMBER (include area code) (410) 436-2914

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PREFACE

The work described in this report was authorized under Contract No. DAAM01-98-C-0008. This work was started in January 1999 and completed in June 1999.

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Acknowledgments

The authors thank Dr. Joseph DeFrank, U.S. Army Edgewood Chemical Biological Center (ECBC), and Rich Matuzsko, GEO-CENTERS, Inc., for procuring samples of the MAXFLIGHT[®] deicing fluid, and Dr. Steven Harvey, ECBC, for discussions regarding HD solubility.

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FEASIBILITY OF FORMULATING DECON GREEN WITH AIRCRAFT DEICING FLUID: VX, GD, AND HD REACTIVITY

1. INTRODUCTION

Suitable replacements for the toxic and corrosive DS2 decontaminant are currently under consideration. Desirable characteristics of the next generation decontaminant include maintaining a broad-spectrum reactivity towards all agents, even in cold weather operations, while achieving a significant reduction in its toxic, corrosive, and environmentally harmful nature. Preliminary work on DECON GREEN [composed of bicarbonate (baking soda), hydrogen peroxide, and alcohol] has shown that this seemingly innocuous concoction is extremely reactive against VX, GB, and HD.¹ The bicarbonate and peroxide effect perhydrolysis of VX^{2,3} and GD⁴ and peroxocarbonate-catalyzed oxidation of HD.⁵ Toxic agent byproducts, namely EA-2192 and mustard sulfone, are not formed.¹ The alcohol functions as a cosolvent and as an antifreeze. Although stable for several hours, DECON GREEN need not be premixed in a holding tank prior to application. Indeed, generation of the reactive OOH^- and HCO_4^- species appears fast enough to permit mixing within the dispensing apparatus.

The present study examines using two aircraft deicing fluids in place of the alcohol in the DECON GREEN formulation. The use of these materials would reduce the logistic burden of the decontaminant. One deicing fluid was an amber-colored solution composed of 40% ethylene glycol, 30% propylene glycol, and 30% water (manufacturer unknown). The second fluid was a green solution (tradename MAXFLIGHT[®], Octagon Process, Incorporated, Edgewater, NJ) containing 50% propylene glycol, 50% water, and a proprietary thickener. The amber fluid is toxic since it contains ethylene glycol. The green fluid is nontoxic since it only contains propylene glycol, a common food additive.⁶

Both deicing fluids contain considerable amounts of water. This precluded the use of aqueous peroxide as the final mixture would possess too high a water content to effectively dissolve HD. Therefore, the solid urea hydrogen peroxide addition compound ($\text{urea} \cdot \text{H}_2\text{O}_2$) was used. Apparently, $\text{urea} \cdot \text{H}_2\text{O}_2$ yields a somewhat acidic solution in water; and in some formulations, sodium carbonate (Na_2CO_3) was used to make the solution more basic than that obtainable with sodium bicarbonate (NaHCO_3) alone. VX perhydrolysis is only fast above pH 8 or 9; whereas, GD perhydrolysis and HD oxidation are both relatively fast near pH 7.

2. EXPERIMENTATION

2.1 Materials.

The $\text{urea} \cdot \text{H}_2\text{O}_2$, NaHCO_3 , Na_2CO_3 , ammonium bicarbonate (NH_4HCO_3), and ammonium carbamate (a mixture of variable proportions of NH_4HCO_3 and ammonium carbamate, $\text{H}_2\text{NCO}_2\text{NH}_4$) were obtained from Aldrich Chemical Company (Milwaukee, WI). The amber deicing fluid was obtained from Maryland Air Guard, Martin State Airport, MD. The NMR analysis of this fluid showed the following composition volume percent (vol %): 40% ethylene glycol, 30% propylene glycol, and 30% water. The green deicing fluid was obtained from Octagon Process, Incorporated (Edgewater, NJ), and is sold under the name MAXFLIGHT[®].

The NMR analysis of this fluid showed that it contains 50 vol % propylene glycol and 50 vol % water. Company literature also indicates that it contains an additional "proprietary thickener" that NMR did not detect.

2.2 Procedure.

The desired amounts of urea•H₂O₂ and bicarbonate/carbonate were added to a 4-mL glass vial. The deicing fluid was then added, and the vial was capped and shaken. The urea•H₂O₂ dissolved instantly and also seemed to assist in the dissolution of the slow-dissolving bicarbonates. A 0.75-mL aliquot was then transferred to a 5-mm NMR tube. The tube was placed in the NMR spectrometer [Varian Unity *Plus* 300, Varian Incorporated, Palo Alto, CA] where tuning and shimming was performed prior to adding the agent. The tube was then removed to a fume hood where appropriate amounts of the agents were added to achieve the desired concentrations: 2 µL VX (0.01M), 1.3 µL GD (0.01M), or 9 µL HD (0.1M). The tube was capped and shaken vigorously to thoroughly dissolve the agent. The sample was then placed back into the NMR spectrometer. About 15 min elapsed between mixing the solution ingredients and adding the agents. This was more than enough time for the reactive species to be generated, as previous studies have shown that this takes place within a minute or so. For VX and GD, ³¹P NMR spectra were taken over time to monitor the reaction and identify intermediates and products. Spectra were referenced to external 85% H₃PO₄ (0 ppm). For HD, ¹H NMR spectra were used, which were referenced to external TMS (0 ppm). Reaction half-lives were determined from the rate of disappearance of the agent peaks in the NMR spectra.

3. RESULTS AND DISCUSSION

3.1 Kinetic Studies.

Half-lives measured for VX, GD, and HD in various formulations using the green MAXFLIGHT® and amber deicing fluids are given in the table. Data from a previous study using t-BuOH as the alcohol co-solvent is also shown for comparison. The data shows that DECON GREEN formulated with either deicing fluid maintains fast reactivity for GD. However, reactivities for VX and HD, while still acceptable, are slower than the formulation with t-BuOH.

More subtle reactivity trends are apparent with regard to the bicarbonate. Compared to NaHCO₃, the somewhat less basic NH₄HCO₃ offers faster HD reactivity, but slower VX reactivity. Conversely, the somewhat more basic ammonium carbonate and NaHCO₃/Na₂CO₃ mixture yields faster VX reactivity, but slower HD reactivity. These observations are consistent with the underlying reaction mechanisms. For VX, perhydrolysis^{2,3} is faster under more basic conditions since the concentration of the reactive peroxyanion, OOH⁻, increases with pH. However, for HD, which reacts via peroxocarbonate-catalyzed oxidation,⁵ the concentration of the reactive HCO₄⁻ species is maximum near pH 7, and decreases with increasing pH.⁷ The HCO₄⁻, an alpha nucleophile, may also be contributing to the observed VX and GD reactivity; however, it is more likely effective against the latter, which still reacts quickly near pH 7. Finally, above about 0.8M bicarbonate concentrations, the reaction rates for VX and HD begin to diminish as a result of phase separation caused by the high salt content.

Table. Kinetic Data for Agents in Various DECON GREEN Formulations

Carbonate	Urea•H ₂ O ₂	Solvent	Half Lives		
			VX (min)	GD (min)	HD (min)
0.5 M NaHCO ₃	4.0 M	MAXFLIGHT [®]	20.7	<1	7.1
0.5 M NH ₄ HCO ₃	4.0 M	MAXFLIGHT [®]	22.0	<1	6.2
0.75 M NaHCO ₃	4.0 M	MAXFLIGHT [®]	40.2	-	4.5
0.75 M NH ₄ HCO ₃	4.0 M	MAXFLIGHT [®]	-	-	7.4
0.8 M NaHCO ₃	4.0 M	MAXFLIGHT [®]	-	-	6.5
1.0 M NaHCO ₃	4.0 M	MAXFLIGHT [®]	47.3	-	16.5
1.0 M NH ₄ HCO ₃	4.0 M	MAXFLIGHT [®]	22.0	-	7.5
1.0 M Ammonium Carbonate	4.0 M	MAXFLIGHT [®]	1.3	-	11.9
0.25 M NaHCO ₃ + 0.25 M Na ₂ CO ₃	4.0 M	MAXFLIGHT [®]	1.2	-	14.8
0.5 M NaHCO ₃	4.0 M	Amber Deice	-	<1	10.5
0.5 M NH ₄ HCO ₃	4.0 M	Amber Deice	-	<1	7.5
0.75 M NH ₄ HCO ₃	4.0 M	Amber Deice	-	-	7.5
0.75 M NaHCO ₃	4.0 M	50 vol % t-BuOH/H ₂ O	7.5	<1	1.6

3.2 HD Solubility.

Over the course of the study, we observed that HD did not readily dissolve when it was added to the various formulations made with the more thoroughly tested MAXFLIGHT[®] fluid and 50 vol % propylene glycol/water. Indeed, vigorous shaking was required to get HD into solution. Other simple alkyl alcohols examined in previous work did not exhibit such difficulty in dissolving HD in the presence of comparable amounts of water. Thus, compared to typical alcohols, diols such as propylene glycol and ethylene glycol are not as effective as co-solvents for HD.

It should be pointed out that the amount of HD challenge (0.1M) was 10-fold higher than the VX and GD challenges (0.01M), and is a contributing factor to the dissolution problem. Although the real world HD challenge level is perhaps uncertain, dissolution of HD at any challenge level may be improved by a number of approaches (e.g., adding a nonionic surfactant). Such surfactants would be completely compatible with the reactive components of DECON GREEN.

3.3 DECON GREEN Stability.

Although not examined in the case of the deicing fluids, DECON GREEN formulations with t-BuOH have maintained their reactivity for several hours. However, long-term stability is not an issue if it is deemed more operationally desirable to mix on the fly using the dispensing apparatus. This would simplify the apparatus by eliminating the need for a mixing tank.

4. CONCLUSIONS

Good reactivity for VX, HD, and especially GD is maintained in DECON GREEN formulated with the two deicing fluids examined. However, simple alkyl alcohols such as t-BuOH still provide faster reactivity compared to the diols contained in the deicing fluids (i.e., ethylene and propylene glycol). Simple alkyl alcohols are also more effective than the diols in the dissolution of HD. If needed, improved HD dissolution could be achieved using nonionic surfactants, which would be completely compatible with the reactive components of DECON GREEN. DECON GREEN may be mixed on the fly using a suitable dispensing apparatus, eliminating the need to premix it in an external holding tank.

Results indicate that DECON GREEN may be formulated with either of the two deicing fluids examined, while maintaining an acceptable level of reactivity for VX, GD, and HD; however, greater reactivity could be realized using simple alkyl alcohols.

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